SCIENCE FOR CERAMIC PRODUCTION

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OBTAINING NANOSTRUCTURED POWDERS OF PARTIALLY STABILIZED ZIRCONIUM DIOXIDE FOR CERAMIC WITH HIGH MECHANICAL STRENGTH

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It is shown that the method of synthesis of precursors by spraying hot highly concentrated with respect to zirconium solutions into concentrated solutions of ammonia permits obtaining in combination with mechanical working under optimal conditions nanopowders of partially stabilized zirconium dioxide (PSZD), from which a ceramic with high mechanical strength (800 MPa) can be obtained even by consolidating powder by semidry pressing. The effect of the synthesis temperature of hydroxides on the characteristics of the powders and ceramic is studied.

Key words: zirconium dioxide, precursor, ceramic, bending strength, nanopowder, morphology, formation, sintering.

Materials based on zirconium dioxide partially stabilized (PSZD) by yttrium, magnesium, and calcium oxides are used to fabricate high-density, high-strength ceramic, refractories, and special-purpose composites — solid electrolytes for high-temperature fuel elements, parts for electrochemical generators and hydroabrasive cutting tools, end seals and valves in pumps for pumping corrosive liquids, milling bodies for "clean" mills, frameworks for dental prostheses, and other applications.

Considering the multistage structure of ceramic technology, where each preceding stage influences the subsequent stages, as well as numerous and often contradictory requirements for powders for ceramic with high mechanical strength (chemical purity, high dispersity, low agglomeration, nearly spherical particle shape, activity with respect to sintering, and others), precursors must be obtained by methods that give the required powder quality already at the initial stages of the technological scheme, especially when the powders are consolidated by semidry pressing and sintering (SDPS). The problem of obtaining high-quality articles from PSZD can be solved by using nanodispersed powders.

Of the large number of known methods of obtaining zirconium hydroxides the most suitable one for obtaining nanopowders of precursors is, in our opinion, spraying a heated highly concentrated solution into water solutions of bases, as developed by E. S. Lukin and colleagues in 1980 at the D. I. Mendeleev Russian Chemical Technology University [1]. The use of the spraying method in combination with mechanical activation of a precursor makes it possible to obtain PSZD powders with particle size of several tens of nanometers [2]. Ceramic with bending strength σ_b to 2500 MPa has been obtained from such powders using additional pressing in a hydrostat and sintering in a gasostat at temperature 1400 – 1500°C [2].

The objective of the present work is to determine the possibility of fabricating ceramic with high mechanical strength by the SDPS method from precursors obtained by spraying solutions [1].

Chemically pure $ZrOCl_2 \cdot 8H_2O$ (OKhTs) was used as the initial zirconium compound. Chemically pure $YCl_3 \cdot 6H_2O$ was used as the compound of the stabilizing element (3%[3] Y_2O_3).

The PSZD precursors — highly dispersed mixed zirconium-yttrium hydroxides — were obtained by spraying a

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[3] Here and below — molar content.

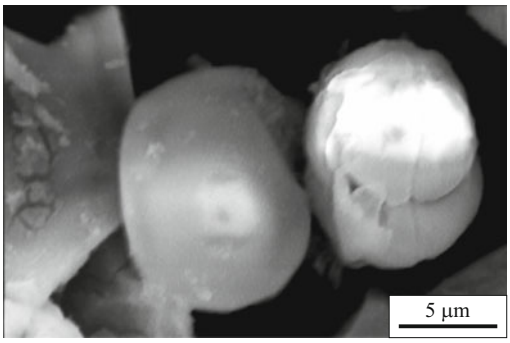

Fig. 1. Morphology of particles in hydroxide obtained by spraying solution, heated to 100°C.

mixture of heated highly concentrated (about 2.5 M Zr) OKhTs solution and yttrium chloride into a solution of concentrated ammonia. The hydroxide obtained was separated from the mother liquor on a Büchner filter, washed with distilled water to a negative reaction on $Cl^?$, dried in a dessicator, and mechanically worked for a short time in a Fritsch "Pulverisette 5" centrifugal planetary mill. The corundum drums were first lined with PSZD (3% Y_2O_3); the balls were made of PSZD (3% Y_2O_3). After disaggregation the powder was heat-treated in an electric furnace at 500°C. After mechanical treatment and disaggregation the PSZD powder was used to form (p_{sp} = 100 – 200 MPa, temporary technological binder — PVC) blanks (40 × 6 × 4 mm bars), which were sintered at 1500°C (the isothermal soaking time at the maximum temperature as 3 h). The calcination losses of the initial zirconium and yttrium compounds and the characteristics of the ceramic (linear shrinkage, porosity, apparent density, and σ_b) were determined by the standard methods [3].

The initial compounds, intermediate products, and ceramic were studied by means of laser granulometry (Analysette-22 "Economy," Fritsch, GmbH), XPA (DRON-3M diffractometer, CuK_α), and differential-thermal analysis (Derivatograf 1500Q) as well as optical (Polam R-211) and electronic (JSM JEOL 5910 VL) microscopy.

The average size of the crystallites was determined using the Scherrer equation [4]. The content of the monoclinic modification V_m was calculated from the equation

$$V_m = \frac{[I_m(111)+I_m(11\bar{1})]}{[I_m(111)+I_m(11\bar{1})+I_t(111)]}, \qquad (1)$$

where I_m and I_t are the intensities of the reflections of the monoclinic and tetragonal phases.

The hydroxides obtained by spraying a solution at 100°C (according to XPA — x-ray amorphous substances) consisted of low-hydrated well-filtering (2.7 $m^3/(m^2 \cdot h)$) precipitates. Electron microscopy (Fig. 1) showed that after drying the hydroxides contained spheroidal aggregates ranging from 5 to 30 μm in size, as well as fibrous (dendritic) aggregates up to 80 μm in size.

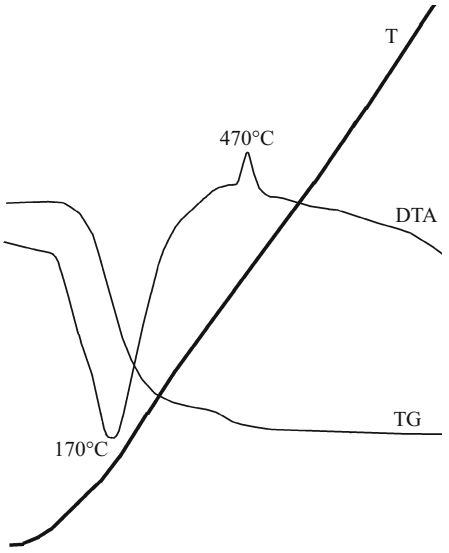

Fig. 2. TG – DTA curves of hydroxide obtained by spraying a solution heated to 100°C.

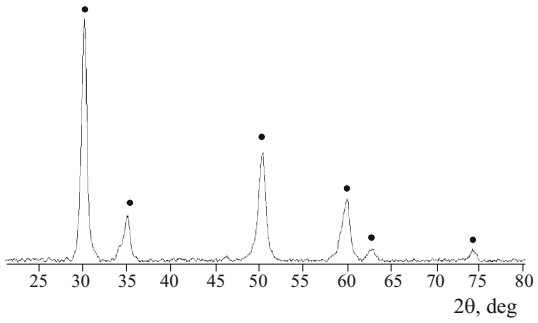

Fig. 3. Diffraction pattern of PSZD powder after heat-treatment at 500°C: ●) *t*-ZrO_2.

The thermogram of a hydroxide obtained by spraying solutions at 100°C (Fig. 2) is typical for hydroxide powders obtained by this method [1]. The deep endothermal effect with an extremum at 170°C (start — 80°C, completion — 320°C) is due to the removal of adsorbed and chemically bound water, while the exothermal effect with an extremum at 470°C is due to the formation of a solid solution.

According to XPA, the PSZD powder from hydroxide obtained by spraying a solution heated to 100°C contains, after heat-treatment at 500°C, only the tetragonal phase of zirconium dioxide (Fig. 3).

The results of electronic microscopy (Fig. 4) show that after mechanical working in R-5 the PSZD powder contains aggregates consisting of 50 – 100 nm nanoparticles.

The samples were made from PSZD powder by uniaxial bilateral semidry pressing under pressure 100 and 200 MPa. The rods obtained were sintered at the same temperature as

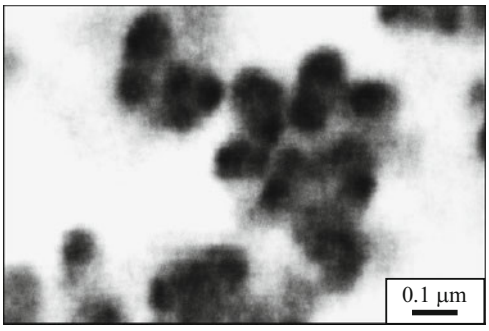

Fig. 4. Photomicrograph of PSZD powder after mechanical working.

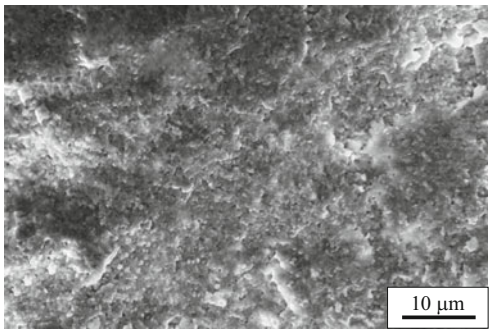

Fig. 5. Photomicrograph of a ceramic chip from a precursor obtained by spraying a solution heated to 100°C.

the samples after additional pressing in a hydrostat [2]. When the pressing pressure was increased from 100 to 200 MPa the density of the compacts increased negligibly — from 48 to 51% of the theoretical value, while the density of the ceramic increased from 89 to 99% of the theoretical value. The results of electron microscopy of a ceramic chip are presented in Fig. 5.

The investigation of the microstructure of the ceramic from the precursor obtained by spraying a solution heated to 100°C showed that the matrix is the tetragonal phase of ZrO_2 with about 0.5 mm grains. The crystals are close to one another, so that the boundary between the neighboring crystals becomes smoothed. The closed porosity does not exceed 1 – 2%.

The results of the investigation confirm the information presented in [2]: spraying solutions heated to 100°C makes it possible to obtain nanodispersed PSZD powders from which a ceramic with high mechanical strength can be obtained even with consolidation by SDPS.

To determine the laws of the process used to obtain PSZD precursors by spraying which are associated with the effect of temperature as well as with inheritance of their microstructure by the PSZD powders and the ceramic, experiments were performed with PSZD precursors obtained at lower temperatures of the sprayed solutions (85 and 70°C).

It was determined that decreasing the temperature of the solution of salts from 100 to 85°C has practically no effect on the filtration rate of the hydroxide precipitates, which was 2.7 $m^3/(m^2 \cdot h)$, while the precipitates of the hydroxides obtained with sprayed solution temperature 70°C filtered even less well — their filtration rate did not exceed 1.6 $m^3/(m^2 \cdot h)$.

Laser granulometry results (Fig. 6) show that the average size of the aggregates in hydroxides (d_{50}) obtained with various solutions temperatures is the same and equals about 30 mm. However, if the sizes of most aggregates (d_{90}) in hydroxide obtained with solution temperature 70°C did not exceed 80 mm, the analogous values for hydroxides obtained from solutions heated to 80 and 100°C were 120 and 110 mm, respectively. The measurements of the granulometric composition of the hydroxides under conditions of ultrasonic treatment (US) of the samples show that when the temperature of the sprayed solution is decreased the aggregates present in the hydroxides become stronger: the average size (d_{50}^{US}) of the particles increasing from about 13 mm (100°C) to 16 – 17 mm (70 and 85°C).

After the precursors are heat-treated at 500°C and then mechanically worked for a short time the average particle size of the PSZD powders obtained with different temperatures of the sprayed solution was practically identical: d_{50} = 2.1 – 2.4 mm (no ultrasonic treatment) and d_{50}^{US} = 1.0 – 1.3 mm (with ultrasonic treatment).

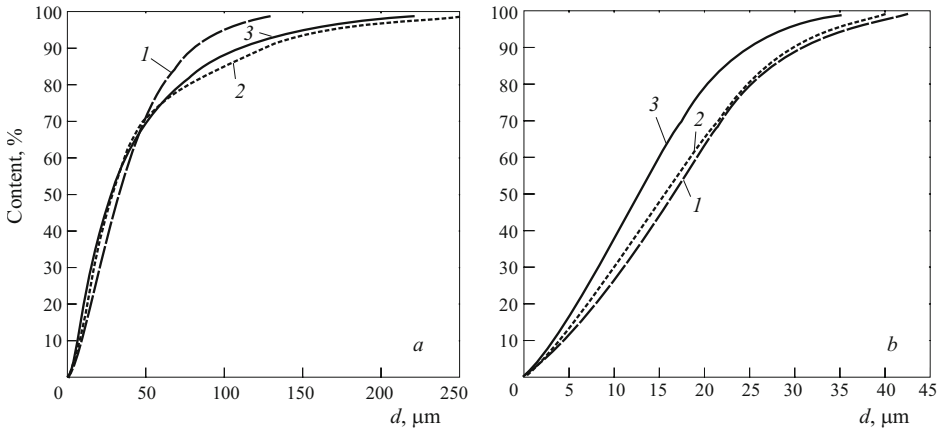

Fig. 6. Integral curves of the size distribution of the particle aggregates in hydroxides obtained with different temperatures of the sprayed solutions: *a*) no US; *b*) with US; *1*) 70°C, *2*) 85°C, *3*) 100°C.

TABLE 1. Effect of the Solution Temperature during Synthesis of the Precursor on the Material Properties

Solution temperature, °C	Density, % theoretical value		Bending strength, MPa
	compacts	ceramics	
70	51.2	92.9	550 ± 50
85	51.0	94.7	630 ± 50
100	50.7	99.5	750 ± 50

According to XPA data the content of the tetragonal phase ZrO_2 (JCPDS No. 79-1771) in PSZD powders (500°C) from hydroxides obtained with sprayed solution temperatures 70 and 100°C differed by approximately a factor of 2 (about 54 and 100%), while the average size of the *t*-ZrO_2 crystallites was the same (about 14 nm).

The decrease of the *t*-ZrO_2 content in the PSZD powders from precursor obtained with the temperature of the sprayed solution lowered to 70°C could be due to the nonuniform distribution of the stabilizing additive.

PSZD powders obtained from precursors obtained with sprayed solution temperatures 70 and 85°C were formed and sintered under the same conditions as the precursor obtained at sprayed solution temperature 100°C.

Comparing the microstructure of ceramic formed from precursors obtained by spraying solutions at 100 and 70°C shows that decreasing the temperature increases the average grain size approximately two-fold (from 0.5 mm to 0.7 – 1 mm) and the closed porosity more than three-fold (from 1 – 2 to 7%).

The results of the investigation which are presented in Table 1 indirectly confirm the inheritance of the ceramic microstructure of precursors obtained by spraying heated solutions. A decrease of the solution temperature from 100 to 70°C when obtaining the precursor is accompanied by a decrease of the strength even with pressing pressure 200 MPa by approximately a factor of 1.5.

Nonetheless, the values of σ_b attained for ceramic obtained from precursors of PSZD nanopowders obtained by spraying and using consolidation of the powders by SDPS fall into the range of values of σ_b for ceramic from powders of precursors (obtained by co-precipitation of OKhTs hydroxides and yttrium chloride) which is prepared at $T \leq 1500$°C by cold isostatic pressing (CIP) or slip casting (Table 2).

The results obtained show that the method of synthesizing precursors by spraying hot highly concentrated solutions of crystal hydrates of Zr and Y salts into concentrated solutions of ammonia makes it possible to obtain, using in addition mechanical working in optimal regimes, ceramic nanopowders with high bending strength even if a method such as semidry pressing is used to consolidate the powders.

TABLE 2. Dependence of the Ceramic Strength on the Consolidation Regimes for the PSZD Powders

Consolidation regimes	Strength σ_b, MPa	Reference
CIP, 0.4 GPa, 1500°C	750	[5]
CIP, 0.1 GPa, 1500°C	720	[6]
CIP, 0.4 GPa, 1500°C	460	[7]
Hot casting under pressure, 1450°C	680	[8]
Slip casting, 1450°C	640	[9]
Slip casting, 1450°C	650	[10]

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